DIFFERENCES AMONG OZOCERITES

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ABSTRACT

Of the unusual organic minerals native to various parts of the world, none are more characteristic than the waxy ozocerites that occur in certain mountainous regions. n-Alkanes longer than those found in typical petroleum waxes have been recognized as the major component. Deposits are now largely exhausted, but nine samples were obtained for examination from the Field Museum and other mineral collections.

Separation by temperature-programmed gas chromatography showed that two pairs of groups of n-alkanes were most abundant: 17 to 21 carbons and 29 to 33 carbons, in which homologs of odd carbon numbers predominated, and 42 to 50 and 58 to 62 carbons, in which even-numbered homologs predominated. Galicia ozocerites belong almost exclusively to the second group, whereas Utah ozocerites are largely mixtures of the second and third.

These favored groups may relate to those previously observed in n-alkanes isolated from petroleum. There the most abundant chain lengths are 11 to 17 and 23 to 29, with odd carbons predominating. The n-alkane patterns suggest three possible sources for ozocerite.

INTRODUCTION

Because of their usefulness and relative abundance, there are no more commonplace minerals than coal and petroleum. Oil shales and tar sands promise to become almost as familiar. A dozen other organic minerals found less frequently now seem peculiar in comparison, especially because most deposits have become depleted or exhausted. Of these, none are stranger than earth wax or ozocerite.

Ozocerite and several similar waxy minerals occur in a hundred places around the world, usually but not always in mountainous areas. Ordinarily it is associated with other organic deposits. Its densest occurance is in Galicia, along the southwestern flank of the Carpathian Mountains, especially near Borislav. Scattered deposits are associated with the Caucasus in Russia, the Wasatch in Utah, and lesser ranges elsewhere. Cumulative world production may have reached as much as a million tons, possibly one-tenth of it in the U.S.A. The biggest use was in leather polishes.

n-Alkanes longer than those typical of petroleum are clearly the characteristic components of ozocerite. The melting points range upwards from those of petroleum waxes, the densities and refractive indices are somewhat higher, and the solubilities in various solvents are much lower. In Borislav ozocerite, at least, branched and cyclic saturates are also present (1). The high losses incurred in refining ozocerite with sulfuric acid to produce ceresins suggest gross admixture with polar substances as well.

Just enough is known about the composition of ozocerite to pose a series of interesting questions. In what manner was ozocerite formed: differently than petroleum, simultaneously with it, or subsequently from it? How can such specific structures as n-alkanes be accounted for: by biosynthesis, migration, alteration, or some other means? Do the n-alkanes in ozocerite correlate with the presence of high-melting waxes in some paraffinic crudes and their absence in some asphaltic crudes? Study of the chain-length distribution of the n-alkanes in ozocerite and comparison with that in petroleum (2) ought to suggest answers to such questions.

The n-alkane distributions of nine samples of ozocerite were accordingly obtained by programmed-temperature gas chromatography. Ozocerites were frequently refined before marketing by melting in boiling water, and are said to be commonly adulterated with cheaper waxes. Evidence for such modifications was constantly watched for.

EXPERIMENTAL

Although ozocerite can no longer be obtained directly from the historical sources, pieces exist in museum collections. Seven samples provided by the Field Museum of Natural History through the courtesy of Mr. B. G. Woodland made up the bulk of the material for the present study. Especially significant was the sample from the Industrial and Agricultural Museum at Warsaw, which carried the description: "Earth wax in unrefined state directly after excavation from the mine. From the Association for Earth Wax and Rock Oil Industry at Boryslaw." Further information on these and two other samples are offered in Table I.

Gas chromatograms were run on a dual Hewlett-Packard 5750 instrument temperature-programmed to 400° C at a rate of 10° per minute. Columns were 6-meter lengths of 3 mm tubing, packed with 3% OV-1 on chromosorb G-HP. Detection was by hydrogen-flame ionization. The ozocerite samples were simply dissolved in carbon bisulfide before running.

Typical chromatograms are shown in the two panels of Figure 1. Time from injection in minutes is given at the bottom and the positions of successive n-alkanes at the top. Inserts show heads and tails in greater detail. Ozocerite H-23 at the top ranged from 16 to 59 carbons, and the Russia ozocerite at the bottom ranged from 13 to 54 carbons. The hold temperature of 400° was reached near 37 carbons with both samples; at this point, about one-third of the Russia ozocerite had emerged, and about two-thirds of H-23.

Successive n-alkanes are clearly the major constituents. Two adjacent doublets near the starts of the curves locate n-heptadecane-pristane and n-octadecane-phytane, which serve as unambiguous counters for the n-alkanes. In addition, n-docosane was occasionally added to provide an internal standard at 22 carbons, and a heavy paraffinic petroleum was run daily as an external standard.

Relative amounts of individual n-alkanes were determined by measuring areas under the successive peaks above the baseline representing the background of unidentified intermediate components. Total amounts of n-alkanes given in Table I are based on estimates of the amounts of background, which increases regularly with column temperature. The n-alkane content of H-23 in Figure 1, for example, is clearly much larger than that of the Russia sample. For comparing ozocerite compositions, logarithmic plots of the amounts of the successive n-alkanes were made for each.

DISCUSSION

Such plots for all ozocerites are presented in the three panels of Figure 2. As was evident in Figure 1, alternate n-alkanes often predominate, especially where the amounts are large and differences are most distinct. Asterisks identify n-alkanes that show clear predominance over adjacent homologs in either the original chromatograms or the logarithmic plots.

In the bottom panel, curves for all three Galicia ozocerites almost coincide. Homologs of 27 to 31 carbons each make up more than about 10% of the n-alkane mixture. The biggest differences occur near the ends: the Standard Oil sample shows a small but distinct second peak at 50 to 52 carbons; the Ward's sample shows a shoulder near 50 carbons, as well as starting three carbons lower; and the Warsaw Museum sample is narrowest and therefore tallest. The Warsaw composition might be duplicated by removing the last 1% of the other samples, perhaps by crystallization from a solvent, but there is no evidence of adulteration.

Near the 27 to 31 peak of Galicia ozocerites, odd-numbered n-alkanes predominate. By 40 to 44 carbons, however, a predominance of even carbons appears. The switch occurs between 37 and 38 carbons, suggesting that the n-alkanes derive from two overlapping sources.

In the middle panel of Figure 2, curves for the three Utah ozocerites are distinctly different. The Kyune sample peaks near 29, and plateaus at 42 to 50, much like the Galicia ozocerites. The Fort Worth sample has a large peak at 33 to 37 and a small one at 60, somewhat like a Galicia curve displaced a few carbons to the right. The Soldier Summit plateau at 33 to 37 and a small peak at 58 to 62 match Fort Worth, but the strong peak at 44 to 48 matches Kyune.

The n-alkane predominances help to sort out the Utah differences. The Fort Worth peak and Soldier Summit plateau at 33 to 37 have odd predominance, whereas the Kyune plateau and Soldier Summit peak at 44 to 48 have even. The only anomaly is that the Fort Worth sample retains its odd predominance beyond the switch at 37 carbons.

In the bottom panel of Figure 2, the three remaining ozocerites are again different. The Pennsylvania sample has a weak peak at 17 to 21 and a strong one at 29 to 33, both with odd predominance. The Russia sample has a plateau starting at 17, a peak with even predominance at 42 to 46, and what may be a shoulder with odd predominance between around 31 to 35. Finally, sample H-23 has a strong peak with odd predominance at 29 to 33 and a plateau with even predominance at 42 to 52. Only n-alkanes with 38 or more carbons show even predominance, and only those with 37 or less show odd.

Ozocerites thus have widely different patterns of n-alkane distribution, yet it is the similarities that are most remarkable. Four ranges are favored: 17 to 21 and 29 to 33-plus with odd predominance, and 42 to 50 and 58 to 62 with even predominance.

Percentages of the ranges represented in each ozocerite are summarized in Table 2. Pennsylvania and Galicia samples consist mainly of the 17-to-21 range, whereas Utah and Russia samples are largely mixtures of the 17-to-21 and 42-to-50 ranges.

CONCLUSION

These ranges appear to relate to those previously found in petroleum, the n-alkanes in several of which show two favored ranges below 35 carbons (2). Compositions of three typical petroleums are plotted logarithmically in Figure 3 in the same way as the ozocerites. The n-alkanes from Darius petroleum simply diminish regularly, with no clear predominance of any carbon numbers. Although a peak occurs at 7 carbons, it probably resulted from separation of natural gas during production and perhaps losses of volatile components afterwards. n-Alkanes from John Creek petroleum peak at 11 to 17 carbons with a strong odd-carbon predominance. Uinta Basin n-alkanes show a plateau at 7 to 13 carbons, and a medium peak with odd predominance at 23 to 29.

Also shown for orientation in Figure 3 are dashed lines for three ozocerites, one from each of the panels of Figure 2. The n-alkanes in ozocerites overlap those from petroleum. Considering the entire range, at least three distinctions can be made: (A) n-alkanes of about 10 to 20 carbons, intermediate in abundance, and with a strong odd preference, relatable to natural fatty acids (2); (B) n-alkanes of almost any chain length, most abundant and without odd or even preference, for which no satisfactory explanation has yet been advanced; and (C) n-alkanes of more than 40 carbons, low in abundance and with a definite even preference, that may be associated in some way with doubling of the odd preference of shorter n-alkanes.

Answers to the questions posed earlier require a knowledge that we do not have of the interrelations among these three distinctions, if indeed three are all there are. An assumption that two independent original syntheses (A and B) and a subsequent transformation (C) occur is helpful. Ozocerite would then be formed from petroleum, in which n-alkanes already exist, probably by a biochemical process that would preserve predominance.

LITERATURE CITED

(1) Kastner, Moos, Schultze Erdöl und Kohle 12 77 (1959)

(2) Martin, Winters, and Williams Nature 199 110 (1963)

TABLE I

DESCRIPTIONS OF OZOCERITES
(obtained from Field Museum, except as noted)

Original Source	Description	Original Donor	Approximate % n-alkanes
Boryslaw, Galacia	Sample No. 110	Ward's Nat. Sci. Estab.	85
Galacia, Austria	--	Standard Oil Company	93
Baryslav, Poland	Note attached	Ind. Ag. Museum Warsaw	82
Bedford, Pa.	Native paraffin	Standard Oil Company	80
Russia	Cast cylinder	Worlds Columbian Expos.	--
Fort Worth, Utah	--	Collected by W. J. McKay	95
Kyune, Utah	Native paraffin	Collected by H. M. Black	89
Soldier Summit, Utah	From mine	*	95
H-23 (Utah?)	Source unknown	**	93

* From University of Illinois; donated by Reino Kallio.
** From Colorado School of Mines; donated by A. S. Houghton.

TABLE II

COMPOSITIONS OF n-ALKANES IN OZOCERITES

Nominal Carbon Range	17-23	29-33	46-50	58-62
Predominance	Odd	Odd	Even	Even
Bedford, Pa.	16	84		
Warsaw (Galicia)		97	3	
Ward's (Galicia)		97	3	
Standard Oil (Galicia)		96	4	
Kyune (Utah)	1	92	7	
H-23	3	70	24	3
Fort Worth (Utah)		69	29	2
Russia	7	13	80	
Soldier Summit (Utah)		18	80	2

FIGURE 1

GAS CHROMATOGRAMS OF TYPICAL OZOCERITES

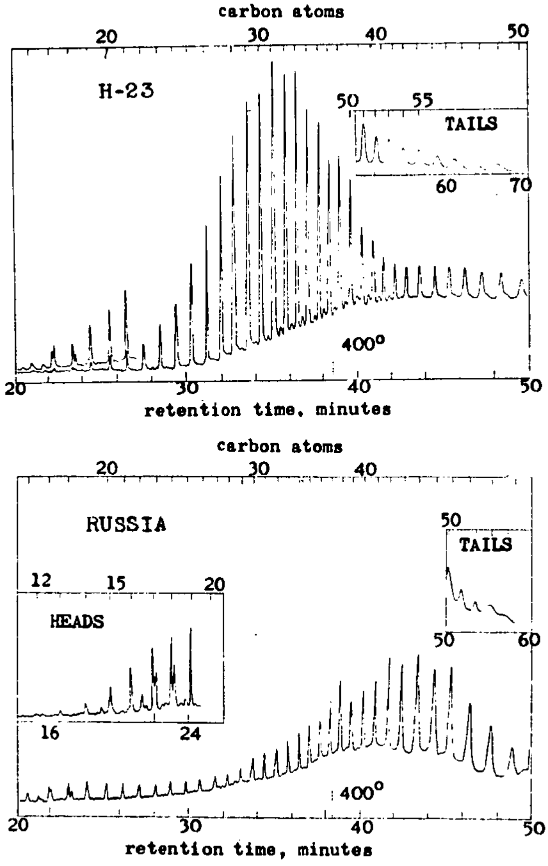

FIGURE 2

n-ALKANES IN OZOCERITES

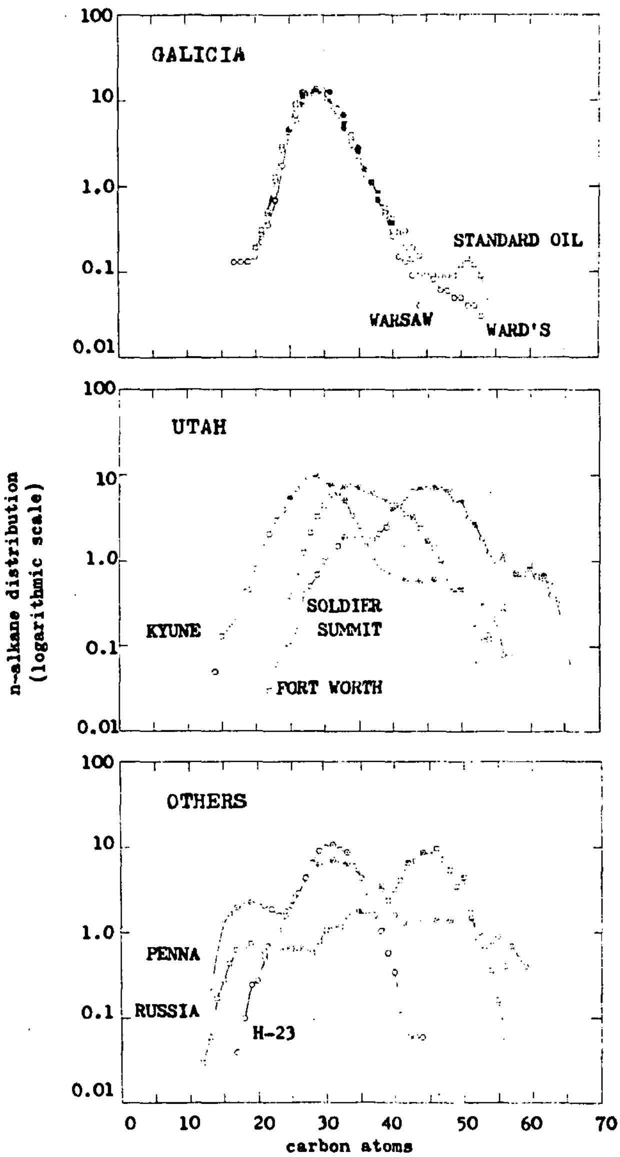

FIGURE 3

n-ALKANES IN PETROLEUM

OVERLAP THOSE IN OZOCERITES